

High-resolution diode-laser spectroscopy on a fast beam of metastable atoms for detecting very rare krypton isotopes

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Abstract. A fast krypton ion beam with an energy of 10 keV is transferred through a mass filter and neutralized in a Rb- (or Cs-) vapour charge exchange cell. The emerging beam of metastable Kr atoms of a selected Kr isotope is collinearly irradiated with a tunable cw GaAlAs diode laser at 811 nm. The spectrum of the $1s_5-2p_9$ transition covers ~ 10 GHz and consists of one line each for the five stable isotopes of Kr with even mass number and 15 hyperfine structure lines of ^{83}Kr . The individual lines are recorded by detecting the fluorescence signal perpendicular to the beams. Photons are guided to the PM tube by diffuse reflection from a high reflectance thermoplastics light collector. Up to 20 photons per atom are emitted by cycling between the two states during the flight time of 1.2 μs through the detector. The observed absorption linewidth of 100 MHz is a combination of laser linewidth and energy uncertainty in the fast atomic beam. In order to achieve maximum isotope selectivity the beam energy has to be adjusted in such a way that the Doppler shifted lines of all isotopes form an optimum pattern for detecting the very rare isotopes ^{81}Kr and ^{85}Kr in natural environmental samples.

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The two rare krypton radionuclides ^{81}Kr (half-life 210 000 yr) and ^{85}Kr (half-life 10.76 yr) occur in Kr samples extracted from air, water or ice with relative isotopic abundances in the range of 10^{-11} to 10^{-14} [1–3]. While ^{85}Kr can be detected in such samples by low level decay counting techniques [4, 5] on Kr samples from several hundred litres of water, no such technique exists for ^{81}Kr . Age dating of very old groundwater and polar ice samples, e.g., is not possible with conventional radioactivity counters.

Accelerator Mass Spectroscopy (AMS) which is very successfully used for other rare radionuclides of importance in geochemistry (^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl , ^{129}I) [6] is not

feasible for noble gas atoms because tandem accelerators operate with negative ions. A recent study with positive ions at the ATLAS linear accelerator facility at Argonne National Laboratory has investigated the possibilities of AMS for detecting ^{39}Ar and ^{81}Kr [7]. For ^{81}Kr the problem of isobaric interference from ^{81}Br needs further experimental work.

An analytical technique based on Resonance Ionization Spectroscopy (RIS) has been developed in recent years for detecting noble gas atoms with isotopic selectivity [8, 9]. Successful measurements of ^{81}Kr extracted from ~ 50 l of old groundwater were reported [10, 11]. The technique makes use of element-selective laser excitation and ionization of the Kr gas in the source region of a time of flight mass spectrometer. Very impressive detection limits below 100 atoms of ^{81}Kr in less than 5 min were achieved [12]. A disadvantage of the new technique, however, is the need for several isotope enrichment steps prior to the final laser atom counting due to the fact that the detection lasers (at 116.5, 558.1 and 1064.0 nm) are pulsed and therefore have bandwidths which are larger than isotope effects in the Kr spectrum.

In the present work, we report experimental results with collinear beam spectroscopy using cw infrared diode lasers irradiating a beam of fast metastable Kr atoms. Such an approach has been proposed by several groups [13–18]. In particular, the rare isotope ^3He [19] and ^{90}Sr [20] have both been detected by similar concepts at concentrations of 10^{-9} to 10^{-11} in natural environmental samples.

The key factor in this technique is the optical isotope shift caused by the Doppler effect between different Kr isotopes moving at the same energy (and therefore with different velocities).

1 Experimental concept

The overall concept is illustrated in Fig. 1. A plasma discharge ion source generates a beam of Kr ions, which are accelerated to 10 keV and focused to pass a Wien filter (crossed E - and B -fields). The mass selected ion beam with

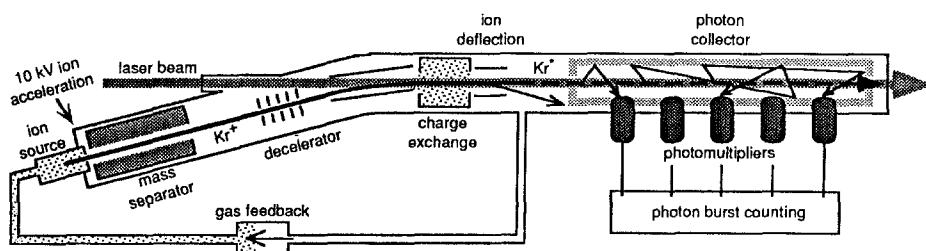


Fig. 1. Overview of the experimental concept. Data reported in this contribution were realized with a simpler test version (see text)

a diameter of ~ 1 mm is decelerated, deflected by a few degrees and enters an alkali vapour charge exchange cell for neutralization. A large fraction of the atoms is thereby transferred into a metastable stage. The remaining ions are deflected and the fast neutral atoms enter the detector where they are irradiated with tunable infrared laser light at 811 nm. An important aspect of our arrangement is the closed vacuum system containing a small turbo pump to recycle the gas between the ion source and the rest of the system. This arrangement allows to work with a very small Kr sample of typically 3×10^{-3} cm³ STP (representing ~ 30 l of groundwater) for several hours [21]. The steady-state pressures are 2×10^{-2} mbar in the plasma discharge ion source and 2×10^{-5} mbar in the rest of the detector system. Getters remove reactive gases.

The experimental results reported in this work were achieved with an earlier version of the detector where the ion decelerator and the small angle beam deflection were not yet realized. Therefore spectroscopic studies with counterpropagating beams at 10 keV ion beam energy only have been possible so far. Furthermore, only one single photomultiplier and a short detector of 18 cm were in use for these first tests.

2 Infrared spectroscopy on metastable Kr at 811.5 nm

A large fraction of the neutralized Kr atoms remains in the $1s_5$ state due to the quasi-resonant charge exchange with alkali atoms [22]. The transition to the $2p_9$ state is highly allowed and can easily be saturated with less than 100 μ W narrow band laser light over a beam diameter of ~ 1 mm.

At 10 keV ion beam energy a ^{84}Kr atom moves at a velocity of 15 cm/ μ s. The Doppler isotope shift is 186.8 GHz under these conditions. With counter-propagating beams the laser wavelength has to be shifted by about 0.41 nm to the red to compensate for the blue shift between atoms and photons. The exact line positions can be calculated from the isotope shifts and hyperfine constants that have been known for some time for the stable Kr isotopes [23–25] but have been measured for this transition only very recently for ^{81}Kr and ^{85}Kr [26]. For ^{81}Kr a sample of ^{80}Kr was enriched in a reactor by neutron activation; for ^{85}Kr a high activity gas was separated from nuclear fission products. With these new data it is now possible to exactly calculate the full Kr spectrum from all natural stable and radioactive Kr isotopes.

Table 1 summarizes the calculated isotope shifts relative to ^{84}Kr for all lines of the even nuclides and the

Table 1. Calculated isotope shifts for all Kr isotopes relative to ^{84}Kr

Line no.	Isotope	Hyperfine transition	Frequency shift [MHz]
1	83	7/2–5/2	– 1408
2	85	7/2–5/2	– 1270
3	83	5/2–5/2	– 1147
4	83	9/2–7/2	– 1132
5	81	5/2–3/2	– 1074
6	85	5/2–5/2	– 1067
7	85	9/2–7/2	– 1060
8	81	1/2–3/2	– 1032
9	81	3/2–3/2	– 1029
10	81	7/2–5/2	– 1008
11	83	3/2–5/2	– 979
12	85	3/2–5/2	– 953
13	81	5/2–5/2	– 837
14	81	9/2–7/2	– 800
15	81	3/2–5/2	– 792
16	83	7/2–7/2	– 753
17	85	7/2–7/2	– 724
18	83	11/2–9/2	– 706
19	85	11/2–9/2	– 688
20	85	5/2–7/2	– 521
21	83	5/2–7/2	– 492
22	81	7/2–7/2	– 397
23	81	11/2–9/2	– 309
24	81	5/2–7/2	– 227
25	78		– 217
26	83	9/2–9/2	– 176
27	85	9/2–9/2	– 164
28	80		– 138
29	83	13/2–11/2	– 87
30	85	13/2–11/2	– 77
31	82		– 64
32	84		0
33	86		66
34	85	7/2–9/2	171
35	83	7/2–9/2	203
36	81	9/2–9/2	463
37	83	11/2–11/2	635
38	81	13/2–11/2	656
39	85	11/2–11/2	703
40	83	15/2–13/2	783
41	81	7/2–9/2	866
42	85	15/2–13/2	870
43	83	9/2–11/2	1166
44	85	9/2–11/2	1226
45	83	13/2–13/2	1744
46	81	11/2–11/2	1967
47	85	13/2–13/2	1986
48	83	11/2–13/2	2466
49	81	9/2–11/2	2739
50	85	11/2–13/2	2766

hyperfine manifolds of the odd nuclides ^{81}Kr , ^{83}Kr and ^{85}Kr . A total of 50 transition lines results. For detecting the rare isotopes ^{81}Kr and ^{85}Kr only their two strongest transitions will most likely be of importance; they are shifted by + 656 MHz ($13/2-11/2$) for ^{81}Kr and by + 870 MHz ($15/2-13/2$) for ^{85}Kr relative to the ^{84}Kr line. It is important to note that both these transitions occur between a perfect two-level system. Excited atoms have no choice but to decay back to the lower state, and therefore atoms can be cycled between the two states by a cw laser beam. With a radiative lifetime of 30 ns [27, 28], an estimated cycling time of 60 ns, each atom will re-emit just about one photon per cm of path (at 10 keV beam energy). At a lower beam energy of e.g. 200 eV and with a possible detector length of (e.g.) 100 cm, up to 700 photons could be re-emitted by each atom while passing through such a long detector. This is an important requirement for a possible detection scheme based on photon burst discrimination [14].

3 The Kr spectrum at 10 keV with counterpropagating beams

In Fig. 2 we present the measured Kr spectrum at 10 keV for the even nuclides (top) and for the odd ^{83}Kr isotope (middle) together with the calculated relative Doppler shift of all lines as a function of the ion acceleration voltage (bottom). The top spectrum was recorded by setting the mass filter to mass 78, followed by scanning the laser over the ^{78}Kr absorption line. The mass filter was then subsequently adjusted to the krypton isotope with the next higher mass before continuing the stepwise laser tuning for each absorption line. For the recording of the ^{83}Kr hyperfine structure spectrum (middle) the Wien filter was set to mass 83. Small fractions of the neighbouring isotopes ^{82}Kr and ^{84}Kr still were allowed to pass the mass filter in order to get markers at the corresponding wavelengths. The calculated isotope shifts for different beam energies (bottom of the figure) are relative to the ^{81}Kr hyperfine manifold at zero energy. In such a picture the strongest ^{81}Kr line ($F = 13/2 - F = 11/2$) which is shift-

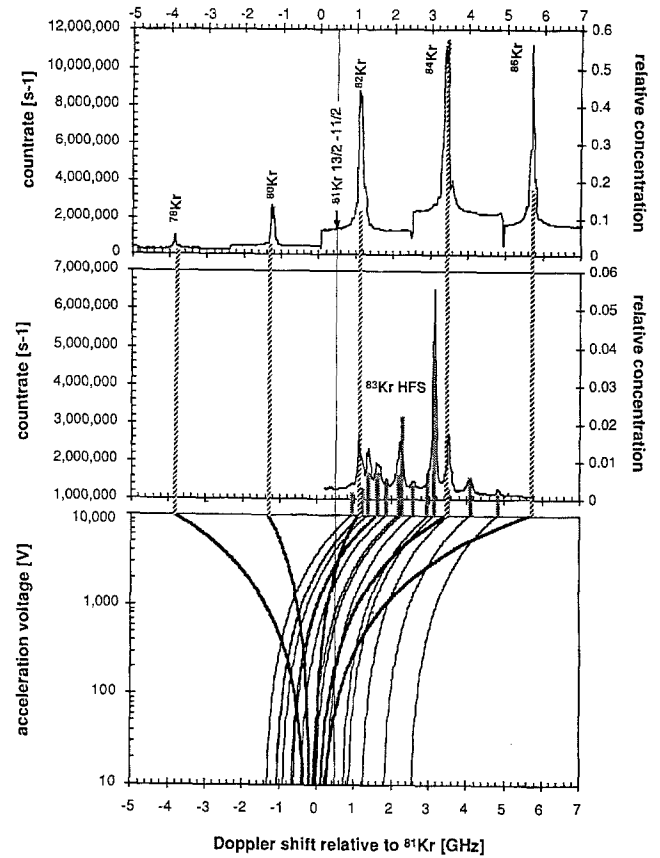


Fig. 2. *Top*: krypton spectrum at 10 keV with counterpropagating beams, even nuclides; *center*: ^{83}Kr hyperfine manifold; *bottom*: calculated frequency shifts of all lines as a function of ion acceleration voltage relative to the ^{81}Kr lines

ed by + 656 MHz relative to ^{84}Kr (Table 1) appears as a vertical line which crosses the curves of the various Kr isotopes illustrating the changing pattern of interference from more abundant isotopes at various beam energies.

In order to maximize optical isotope selectivity the ^{81}Kr line has to be moved away from other lines as far as possible by selecting the proper ion beam energy. In Fig. 3,

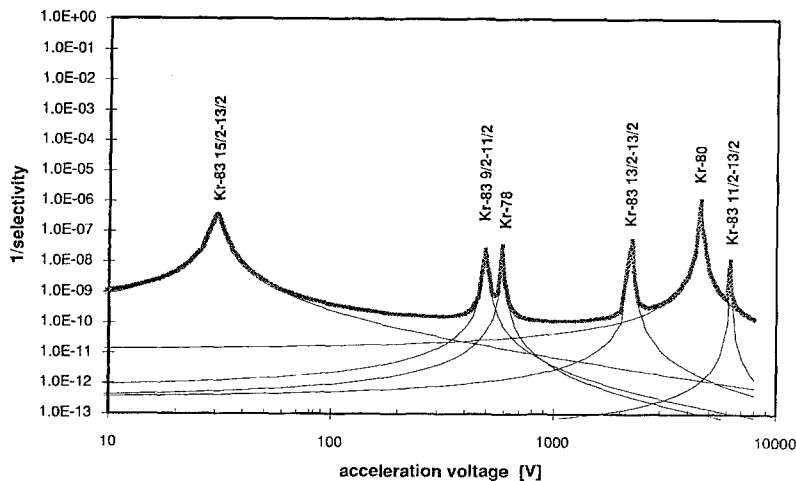


Fig. 3. Inverse selectivity for detecting the ^{81}Kr ($13/2-11/2$) absorption line calculated for copropagating beams and mass separation in a $15''$ Wien filter (see text)

we have calculated the best regions of beam energy for the selective excitation of ^{81}Kr . For copropagating beams, ranges between 100 and 400 eV, between 800 and 1200 eV and above 9 keV appear to be best suited for such work. For calculating the theoretical selectivities in Fig. 3 we have made the following assumptions:

- (1) Wien filter abundance sensitivities relative to mass 81 are 20 000 for ^{80}Kr and ^{82}Kr and 100 000 for all other stable Kr isotopes. These factors were realized with a 15" filter by our colleagues in Oak Ridge [29]. The 6" Wien filter in our current experimental arrangement operates with factors that are 1 to 2 orders of magnitude lower.
- (2) The line profiles are Lorentzian with a natural width (FWHM) of 5.3 MHz corresponding to the excited-state lifetime of 30 ns.
- (3) All abundances of stable Kr isotopes are those of a natural Kr sample.

As can be seen in Fig. 3 the most interfering line for ^{81}Kr at 10 keV as well as at 800 eV is the ^{80}Kr line. Under optimal conditions the present concept should reach a combined isotope selectivity of mass filter and selective optical excitation of 10^{10} .

4 Sensitivity and selectivity

To discuss the various factors which influence the sensitivity and selectivity of detection we refer to Fig. 4. The ^{78}Kr line (with an isotopic abundance of 0.35% in atmospheric krypton) was recorded with a laser scanning of 10 MHz/channel and a data accumulation time of 0.3 s/channel. The width of the line (FWHM) is approximately 100 MHz, the frequency scale being calibrated with a confocal Fabry-Perot interferometer with a free spectral range of 250 MHz. The "satellites" in the line profile must be caused by instabilities of the detection system. A 10 MHz variation during the sampling time of 0.3 s can be caused by:

- (1) an energy fluctuation of 1 eV of the ion beam (relative to 10 000 eV beam energy);
- (2) a temperature instability of 0.33 mK in the diode laser (at the operating temperature of 32°C and with a characteristic temperature tuning of 30 GHz/K);
- (3) an instability of 3 μA in the diode-laser current (at the operating current of 70 mA and with a current tuning rate of 3.3 GHz/mA).

The spectrum was recorded with a neutral current at mass 78 of 0.12 nA (or 7.5×10^8 atoms/s). The recorded net count rate of 2.58 MHz at the peak therefore corresponds to a detection efficiency of 0.0034 counts per ^{78}Kr ion (or 21.5 MHz/nA). This overall efficiency is a product of the following factors: f_1 : efficiency of charge exchange of ions into the metastable $1s_5$ state; f_2 : efficiency of optical excitation, mainly determined by the geometrical overlap of laser beam and atomic beam including their respective shapes; f_3 : efficiency of light collection from the linear source of 18 cm length; f_4 : photomultiplier efficiency at 811.5 nm; f_5 : maximum number of

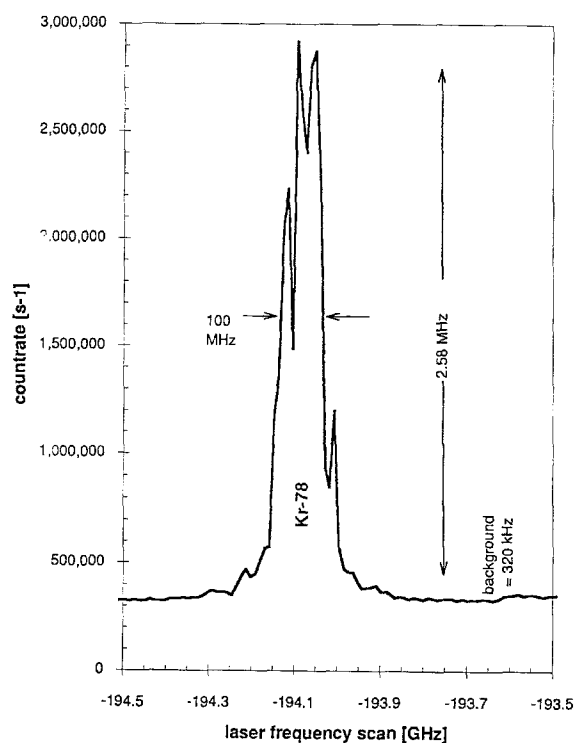


Fig. 4. ^{78}Kr absorption line, counterpropagating beams at 10 keV

photons re-emitted per atom during the flight time through the detector.

The individual contributions cannot easily be determined separately with the present set-up. The following values are our current best guesses:

$$f_1 \times f_2 \times f_3 \times f_4 \times f_5 = 45\% \times 30\% \times 7\% \times 1.8\% \times 20\% \\ = 0.0034 \text{ photons/atom.}$$

The following comments must be made: The measured neutralization efficiency can reach 80% or more but it is currently not known what fraction of the atoms is converted to the $1s_4$ state (which would be lost for the detection) and what fraction may even be lost to the ground state, e.g., by collisions. The quoted overlap efficiency of $f_3 = 30\%$ between atomic and laser beam certainly can be improved; however, in practice it is not easy to exactly overlap an infrared laser beam with a beam of neutral atoms while minimizing the stray light of the laser of the photomultiplier. A factor of $f_2 = 100\%$ would represent a situation where every metastable atom re-emits the maximum of 20 photons on its way through the detector. The light collection efficiency was realized in a prototype detector using multiple diffuse reflections in a high reflectance thermoplastics (Spectralon, reflectance = 99.1% at 800 nm) to guide photons from the inner walls to the photomultiplier which has an active area of 17 cm² (RCA 8852) and which is currently positioned at a distance of 16 cm from the beam axis. Unfortunately the photocathode responsivity in this spectral region is at most 2%. Although we have no direct proof of the cycling of atoms between the two hyperfine levels, we consider the measured detection efficiency presented above together with the best guess of values for the various factors as indirect

evidence that cycling actually occurs. Without any cycling unrealistically higher values for other parameters would otherwise have to be postulated.

Other parameters which are important for a future use of such a technique for ^{81}Kr analysis can also be taken from Fig. 4. The background count rate of 320 kHz has three components:

- (1) photomultiplier dark count rate = 4 kHz (cooled to approx. 5°C);
- (2) count rate from photon emission caused by collisions between fast atoms and residual gas molecules in the system is 36 kHz (equivalent to ~ 500 kHz per nA neutral current) and
- (3) stray light = 280 kHz. This last component currently limits the detection sensitivity of our system and needs to be decreased in the next steps of system development. With the small angle ion beam deflection it will be possible to exactly guide the laser beam through the vacuum system and absorb the energy in a better defined target than in the present preliminary arrangement.

5 Outlook

It is our goal to increase the detection sensitivity to a level above 1 photon/atom in order to be able to apply the discrimination methods demonstrated for photon burst detection [16, 17, 30, 31]. By slowing down the atoms to 200 eV and increasing the detector length to 100 cm each atom will be exposed to photons 40 times longer than in the present experiment. A maximum of 800 photons can be re-emitted by each atom under these conditions. The second-generation light collector which is currently under construction therefore has to reach an overall photon collection efficiency of at least 50%.

It is anticipated that in the final version of a detector for the rare noble gas nuclides ^{81}Kr and ^{85}Kr in environmental krypton samples the required isotope selectivity of 10^{12} or better will be distributed in about equal parts to (1) isotope separation in the ion mass filter, (2) optical isotope selectivity in the Doppler shifted spectra of fast metastable atoms and (3) photon burst discrimination against remaining more abundant stable atoms and stray light.

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